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FLUIDIZED BED COMBUSTION OF NEW BRUNSWICK HIGH SULPHUR COAL AND OIL SHALE

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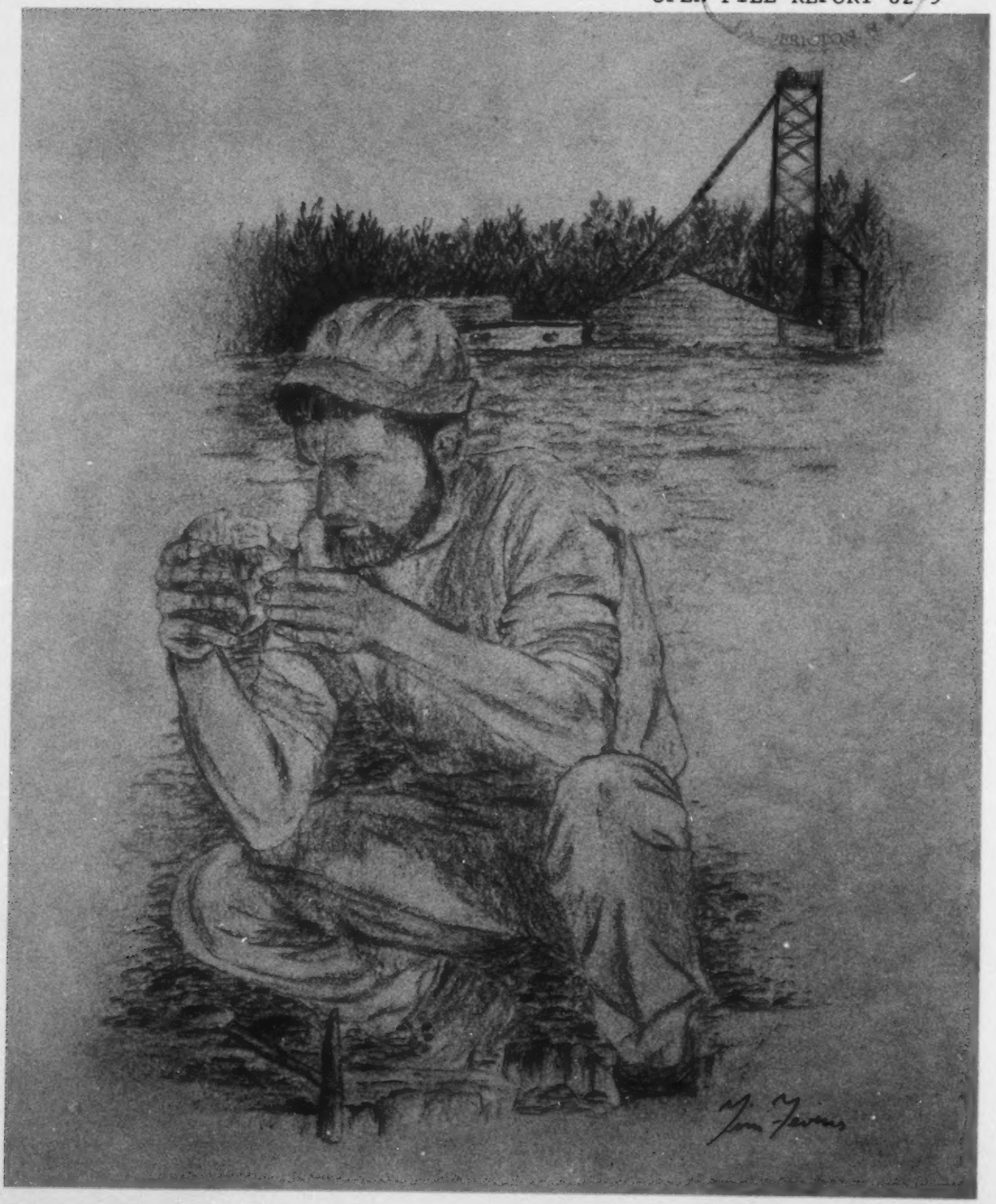

NATURAL RESOURCES
NEW BRUNSWICK
RESSOURCES NATURELLES
NOUVEAU-BRUNSWICK

Government of Canada
Regional Economic Expansion

Gouvernement du Canada
Expansion Économique Régionale

FLUIDIZED BED COMBUSTION
OF
EW BRUNSWICK
HIGH SULPHUR COAL AND OIL SHALE

This is a Federal-Provincial Development Project, Funded Under the Minerals and Fuels Subsidiary Agreement of the Canada-New Brunswick General Development Agreement by the Government of New Brunswick and the Department of Regional Economic Expansion of Canada.

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1.0 INTRODUCTION

1.1 Background

The Mineral Development and Processing Department at RPC was requested by Mr. Don Gemmell, Department of Natural Resources, Mineral Development Branch to investigate the possibility of fluidized bed co-combustion of New Brunswick's high sulphur, high ash coal with Albert County Oil Shale.

New Brunswick possesses large reserves of bituminous coals characterized by high ash and sulphur contents. The calorific value of this material is in the range of 9610-14, 100 Btu/lb, however, the sulphur content of about 7% limits the application of this material as a fuel because of environment control costs due to SO_x emissions.

Large reserves of Carboniferous dolomitic oil shales exist in Albert County in New Brunswick. Analyses of drill cores from the Albert County Formation vary widely, however, the kerogen content is in the order of < 10 to 50 gal/ton forming up to 30 to 40% by volume of the rock at an estimate gross calorific value of 1000-5000 Btu/lb and carbonate concentrations are in the order of 10-40% by weight of $Ca/MgCO_3$.

There has been a great deal of recent interest in coal fluidized-bed boilers. Enthusiasm for fluidized-bed combustion is largely based on its potential for burning coal without the need for scrubbers to clean up flue gas. Early estimates by other workers predict a modest reduction in capital and operating costs over conventional boilers. Limestone addition is the key element in fluidized bed coal combustion. Coal particles are burned in a bed of limestone through which air is passed. As the velocity of air is increased the bed behaves as a boiling fluid. The SO_2 generated from the burning coal is captured by the limestone to form calcium and magnesium sulphate. Steam generating coils are submerged directly into the fluid bed where maximum heat transfer occurs.

Fluidized-bed coal combustion thus has the advantage of reducing SO_2 emissions. The optimum temperatures for this exchange reaction are well below the melting temperatures of ash. The fluidized-bed then has a good potential for treating the high ash New Brunswick coals without the corrosion and stickiness problem generally associated with ash carryover. The operating temperatures are also below 870°C thus reducing the NO_x emissions.

The boilers size and its efficiency for sulphur capture and steam generation are related to many variables including carbonate to sulphur ratios, fluidizing velocities, temperatures, retention times, etc.

Recent studies (1) on oil shales have shown that oil shales are capable of fixing sulphur when they are burned with high sulphur coal in fluid bed reactors at 800°C. When the molar ratio of CaO/S was 2.5:1 about 90% of the sulphur was fixed and the system was in compliance with the environmental protection standards. The hydrocarbon content actually augumented the fuel value of the coal. On the assumption that New Brunswick oil shales would be equally effective per unit of Ca/MgO, then approximately 2 to 3 tons of oil shale would be required per ton of New Brunswick coal burned.

For limestone/coal systems, the required stone/coal ratio would be in the range 1:1 to 2:1, depending on the porosity and reactivity of the limestone, for sulphur capture of New Brunswick high sulphur coals(7%). Doyle showed that lower CaO/S ratios are required for effective sulphur fixation for oil shale than for limestone due to differences in porosity, carbonate grain size, and catalytic component composition and distribution. Also,since limestone has no calorific value and the sulphur fixation reaction is endothermic, limestone addition decreases the fuel value of the coal.

(1) J. B. Doyle "Fluid Bed Combustion of Coal-Oil Shale Mixture". The Combustion Institute, Baton Rouge, Louisiana, March 1980.

The use of oil shale/coal systems over limestone/coal has several advantages.

1) greater steam production/ton of coal.

2) greater benefits derived from fuel conservation measures such as combustion air preheating.

3) possibilities of developing a crude oil feedstock for local refineries.

4) possibilities for recovering values from ash such as mineral byproducts.

5) overall increase in New Brunswick's energy reserve base.

1.2 Objectives and Scope of the Study

The objective of this project was to test the economic and technical feasibility of burning high sulphur, high ash New Brunswick coal in a fluid bed for steam generation. New Brunswick Oil Shales would be tested as an additional supply of thermal energy and as a desulphurizing agent in the coal combustion system.

It was proposed (2) that the following studies be undertaken:

1) A preliminary paper study would be undertaken to estimate the heat and mass balances in a fluidized bed furnace fuelled with NB high sulphur coal and oil shale of specified composition. Projected sulphur emissions and available thermal energy would then be defined and the logistical problems of fuel supply and flyash disposal scoped. Possibilities for byproduct manufacture would be indicated and a preliminary profitability analysis would be prepared.

(2) Research Proposal, "Fluidized Bed Combustion of High Sulphur Coal and Oil Shale", RPC Report No. MDP/80/22.

2) Samples of oil shale will be subjected to differential thermal analysis and thermogravimetric analysis to determine their thermal and ashing characteristics. These are important factors determining the tendency for clinker formation and the tendency for furnace bed defluidization.

3) Preliminary combustion tests will be carried out in the Councils fluid bed roaster to determine fluidization characteristics of coal/oil shale mixtures to check thermal balances and sulphur capture. In these tests, furnace temperatures will be controlled by direct water spray or by cooling coils(at extra cost).

The preliminary paper study is presented as Appendices 2 and 3 in this report. Studies of byproduct manufacture, other than shale oil or upgraded oil shale, and profitability analyses were determined to be premature, any results being meaningless without prior experimental work and ash production for analyses.

Differential thermal analyses and thermogravimetric analyses were proven unnecessary for the preliminary experimental program since it was shown, early in the test program, that combustion bed fluidization characteristics with oil shale and the coal/oil shale mixtures tested were excellent. These analyses have been postponed to the optimization test program which is the next phase of the project.

Preliminary combustion tests in the Council's 6" fluid bed reacter were carried out. Fluidization characteristics of coal/oil shale mixtures, thermal balances, and sulphur capture were examined. Results and discussions of this experimental program are given in Section 4.0 and Appendix 1.

2.0 SUMMARY

Combustion tests on 25 gal/ton Albert Mines Oil Shale have been undertaken in a bench scale rotary tube furnace and a six inch fluid bed reactor tc determine maximum sulphur capture and fluidization characteristics. Rotary furnace trials have shown that oil shale is effective in fixing SO_2 with a maximum utilization of 70 to 79% of the available carbonate at 750-800°C and with retention times of 30 to 180 minutes. This would give an approximate ratio of oil shale required to fix the sulphur dioxide generated from combustion of high sulphur(7%)coals of three parts oil shale to one part coal.

Fluid bed trials on SO_2 capture have indicated even higher fixation ratios and thus higher coal/oil shale ratios (> 1:3) may be possible. Twenty-five gal/ton oil shale in itself gave excellent fluidization characteristics, and produced excess heat over that required to sustain the reactor at 800°C. Cooling water was required to maintain temperature.

Preliminary coal/oil shale blend (1:3) combustion trials were carried out in the 6" reactor. Fluidization was excellent, with dust carryover minimal. Fluidization was enhanced by the coal reaction product of porous pellets consisting mainly of ash. Sulphur dioxide was not detected in the off gas, indicating that higher coal/oil shale ratios (> 1:3) are possible.

3.0 CONCLUSIONS AND RECOMMENDATIONS

The work summarized in this report was undertaken as a technical feasibility study on simultaneous combustion of New Brunswick coals and oil shales. Fluidized bed combustion equipment and experimental techniques were developed and proven experimentally. It was shown that fluidized bed co-combustion of New Brunswick oil shales and coals is technically feasible due to the excellent fluidization characteristics of the materials, high reactivity of sulphur capturing species in the shale, and the ability of the shale to reduce fly ash generation. It was shown that a oil shale:coal ratio of less than 3.0:1 will be sufficient to decrease sulphur emissions to environmentally acceptable standards during the burning of 6.8% S coal. A high precentage of the fly ash generated from the coal combustion was fixed in easily handled hollow pellets discharging in the bed overflow.

A more extensive data base is required to optimize combustion and generate complete mass and energy balances. This information will allow the quantifying of the economic feasibility of burning coal/oil shale blends in a fluid bed reactor for sulphur capture, steam generation, and oil recovery. Therefore, the following test programs are recommended:

1) Optimization trials in the 6" reactor should be carried out varying the coal/oil shale ratio(1:1-1:3), retention times (0.25 hrs-2.0 hrs)and air factor(10-20%). Shale ash and coal ash would be analyzed both chemically and mineralogically to determine extent of feldspar decomposition, sulphur capture on feldspar components, and possibilities of byproducts recovery.

2) After optimum conditions of fluid bed combustion of coal/oil shale blends have been determined some scale up testing should be undertaken in RPC's 14" reactor to obtain data required for an accurate thermal balance.

3) Some experiments should be undertaken in the 6" reactor to test the feasibility of burning low grade oil shale(10 gal/ton) and coal/oil shale feeds.

4) Testing of high spacial velocities in the range of 150-200 cm/sec should be undertaken to reduce retention times and to test coarser feeds(up to ¼"). This data is necessary for scale up and plant capital cost and grinding cost estimations. This will require some conversion of existing equipment to handle, higher velocities and material throughput.

5) The possibility of producing either an upgraded oil shale or a crude oil by means of a fluid bed oil shale retort using flue gas from a conventional coal burning station(0.5% SO_2, 5.0% O_2, 74.9% N_2, 12.0% CO_2, 7.6% H_2O)as the fluidizing media should be investigated. As the hot flue gas passes through a high grade(25 gal/ton)oil shale bed less than 25% of the kerogen would be burned providing some extra heat for volatilization for the remaining kerogen. This vapour carried in the off gas would be condensed and trapped either in oil shale fines blown out of the reactor in the off gas, thus producing an upgraded oil shale for combustion or further treatment for oil recovery, or directly as a crude oil. The SO_2 in the flue gas generated from the coal combustion will be fixed and removed in the shale ash. The conventional expensive scrubbing systems required to meet emission control standards when burning higher sulphur coal could thus be replaced with a fluid bed oil shale-retort which would operate exothermally as compared to lime or limestone systems which are endothermic and would produce a high calorific value fuel, namely oil or upgraded shale oil, as a byproduct.

4.0 EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1 Sample Collection and Preparation

New Brunswick Department of Natural Resources provided oil shale samples by drilling a 600' diamond drill hole in the Albert County Formation. A high grade bulk sample was prepared by blending a crushed and screened fraction from the 400' to 600' level. The sample averaged about 25 gal/ton kerogen. Analyses are given in Table 1.

A minus 50 mesh size oil shale was prepared for preliminary combustion tests after minimal fluidization velocities for various grinds were determined. The results of the room temperature fluidization tests are given in Table 2.

A bulk sample of Minto Coal was selectively screened to 8 mesh and dried. Ultimate analyses of this sample are given in Table 1.

4.2 Sulphur Fixation Chemistry

The chemical reactions are simply exchange reactions where SO_2 replaces CO_2 in the presence of O_2 to form gypsum.

$$CaCO_3 + SO_2 \longrightarrow CaSO_3 + CO_2 \qquad (1)$$

$$CaSO_3 + 0.5O_2 \longrightarrow CaSO_4 \qquad (2)$$

Analogous reactions occur for such as magnesium carbonate ($MgCO_3$) and sodium carbonate (Na_2CO_3).

TABLE 1
Bulk Samples Ultimate Analyses(WT % Dry)

#	Sample	Mineral Carbon	Organic Carbon	Hydrogen	Sulphur	Oxygen	Nitrogen	Ash	Ca**	Mg**	Na**
1	Oil Shale	2.85	12.69	1.98	1.13	7.93	<0.20	72.60	7.3	1.3	0.2
*1a	Oil Shale	2.91	13.13	2.02	1.11	7.29	<0.20	72.72	7.5	1.4	0.1
2	Coal	<1	49.77	3.53	6.80	8.30	<0.20	30.40			
*2a	Coal	<1	54.26	3.83	6.90	0.29	<0.20	33.52			

* 1a is a duplicate sample of 1.

2a is a duplicate sample of 2.

** Weak acid soluble species, ie. present as carbonates in shale.

TABLE 2

Minimum Fluidization Velocities at 25°C for Various Oil Shale Grinds

Mesh Size	Apeture (in)	Minimum Fluidization Velocity (cm/sec)
-100	<0.0058	bed channeling
-50	<0.0117	22 - 29
-42	<0.0139	36 - 55
-20	<0.0328	73 - 100
-14	<0.046	131 - 146
- 8	<0.093	171 - 182
- 5	<0.157	220 - 250
-¼"	<0.225	300 - 350

Earlier work(3) has shown that sulphatization of Mg and Ca minerals occurs readily at 700° in presence of strong SO_X gases with retention times of seven hours.

TABLE 3

U.S.B.M. Sulphatization Trials

	T°C	% Sulphatized
CaO	700	86.3
$CaCO_3$	700	99.2
MgO	700	53.8
$MgCO_3$	700	88.8

Doyle (1) also showed that carbonaceous Colorado Oil Shales could be successfully burned with high sulphur coal with minimal SO_2 emissions.

(3) U.S.B.M. R16514 "Sulphatization of Mn Minerals and Selective gangue minerals".

4.3 Sulphur Fixation in Tube Furnace Trials

In order to determine the sulphur fixing capacity of Albert county oil shale, bench scale testing was undertaken in a rotary tube furnace(Figure 1). Twenty-five gram charges were placed in a one inch by six inch sample tube. It was then immersed into the heated zone of a two inch horizontal furnace. The sample tube was rotated as a stream of pure SO_2 gas was passed through the charge. Samples of both fresh and burned oil shale were subjected to a pure SO_2 gas flow 2.5 times stoichiometric to mineral carbon with retention times of 0.5 to 3.0 hours and temperatures of 600 to 800°C. The results of this work are given in Table 4.

4.3.1. Tests on Oil Shale with Kerogen Removed.

Fresh oil shale samples were heated for 5 hours at 500°C in a muffle furnace to remove organic carbon. This was necessary since accurate analyses of mineral carbon(carbonate)could not be obtained on fresh oil shale samples due to interference by organic carbon. At 600°C a maximum sulphitization* of 46% of mineral carbon species was attained. At 750°C, a mineral carbon utilization of 70% was calculated at both 0.5 and 3.0 hour retention times. A maximum of 79% sulphitization was attained at a temperature of 800°C with a retention time of three hours. The measured SO_2 fixation for this test was 5.80 gm SO_2 fixed per 100 gm of heated oil shale, equivalent to 4.64 gm SO_2 per 100 gm of fresh oil shale.

4.3.2. Tests on Fresh Oil Shale Samples

In general, tests with fresh samples gave only low utilization of CO_3 due to a masking effect of organic carbon from incomplete kerogen burn due to the zero oxygen atmosphere in the tube furnace. Results are given in Table 4. In actual fluid bed combustion, oxygen is present in slight excess and therefore very little or no residual carbon is expected and masking will be minimized

* defined according to equation(1),Section 4.2 assuming no sulphitization of feldspars in the shale.

FIGURE 1

BENCH SCALE ROTARY TUBE FURNACE

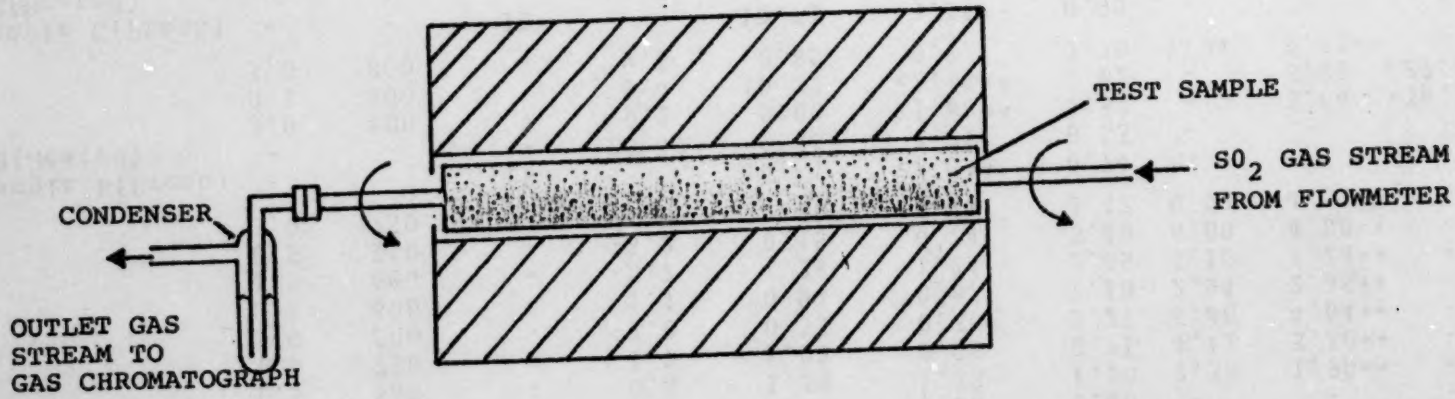


TABLE 4
OIL SHALE SULPHUR FIXATION IN
BENCH SCALE ROTARY FURNACE TRIALS

Sample#	Ret.Time (HRS)	T (^{o}C)	Grade (G/Ton)	WT Loss %	%C Total	%CO_3	S Total	SO_2 Fixat+ (gm SO_2/ 100 gm heated shale)	SO_2 Fixat++ (gm SO_2/ 100 gm fresh shale)	%$CaCO_3$ Utiliz. from fresh shale	%$CaCO_3$ Utiliz. from heated shale
Shale Sample A(Fresh)	-	-	25	-	16.72	<2.72**	0.70	-	-	-	-
Sample A(Heated)	-	-	-	20.7	1.70	1.60	0.60	-	-	-	-
SF1	1.5	600	-	0.8	1.38	1.33	1.80	2.38	1.90++	-	16.8
SF2	1.5	750	-	1.7	1.02	0.95	2.71	4.12	3.30++	-	40.6
SF3	3.0	800	-	-7.0	0.33	0.33	3.27	5.80	4.64++	-	79.4
SF4	0.5	600	-	1.4	0.94	0.87	2.10	2.94	2.35++	-	45.6
SF5	1.5	600	-	-0.2	1.28	1.24	2.05	4.10	3.28++	-	22.5
SF6	0.5	750	-	-3.2	0.45	0.24	3.49	6.00	4.80++	-	69.7
SF7	3.0	750	-	-4.0	0.50	0.45	3.47	6.02	4.81++	-	69.2
Shale Sample B(Fresh)	-	-	25	-	16.60	<3.3**	0.74	-	-	-	-
Sample B(Heated)	-	-	-	20.37	2.85	2.75	0.53	-	-	-	-
SF8*	3.0	800	-	9.2	5.00	<1.88**	2.82	-	3.64	>36.7	-
SF10*	0.5	800	-	9.4	10.32	<2.12**	2.82	-	3.62	>27.2	-
SF12	3.0	800	-	9.5	0.85	0.77	3.70	7.04	5.63++	-	70.6
Shale Sample C(Fresh)	-	-	10	-	10.72	<3.3**	0.90	-	-	-	-
Sample C(Heated)	-	-	-	14.0	3.28	3.08	0.73	-	-	-	-
SF9 *	3.0	800	-	9.7	2.20	<1.05**	4.60	-	6.50	>66.9	-
SF11*	0.5	800	-	9.0	5.22	<2.24**	2.42	-	2.60	>34.6	-

* Sulphur Fixation tests done on fresh shale samples, all others performed on shale samples that had been previously,heated to 500^{o}C for 5hr to drive off organic carbon prior to sulphur fixation testing

** These must be considered as maximum values due to interference of high organic carbon in sample on mineral carbon assays.

\+ Based on SO_2 absorbed from gas, does not include S present in shale.

++ Calculated from weight loss on heating.

Sulphitization would also be increased in fluid bed conditions as the grain to gas contact is maximized.

The results of this work indicated a maximum carbonate utilization in the range of 70 to 79%. With the Minto Coal sample, having a sulphur value of 6.8%, the approximate maximum coal to oil shale ratio for optimum sulphur fixation would be in the range of 1:3.

4.4 Sulphur Fixation in 6" Fluidized Bed

4.4.1. 6" Fluid Bed Design

Preliminary fluidized bed tests were conducted in RPC's 6" fluidized bed reactor system which is illustrated in figure 2.

The system is made up of several interdependant sub-systems. The fluidized bed reactor is composed of two SS316 sections bolted together and measures five feet high. Preheated air is distributed into the reactor through mushroom-type tuyeres. Ash is removed from the bed by means of an overflow pipe located on the side of the reactor at a height of 15", leaving a freeboard height of 48". External coils on the reactor and preheated air are used initially for startup. Two single loop cooling coils are used to control bed temperatures.

The gas cleaning system consists of two cyclones in series. The cyclones discharge through a rotary star valve. The dust separated in the gas cleaning system is then returned by gravity to the reactor through the dust return pipe.

The off gasses and dust carryover are sampled by means of a gas chromatograph, a wet SO_2 analyser, and a 1" cyclone dust trap.

The feeding system consists of a carbon steel screw feeder bin mounted on 4 pressure transducers for gravimetric feed control. Oil shale and coal/oil shale blends were fed pneumatically to the reactor from the volumetric screw feeder. Feed transport air was minimized to prevent spouting and bed short-circuiting.

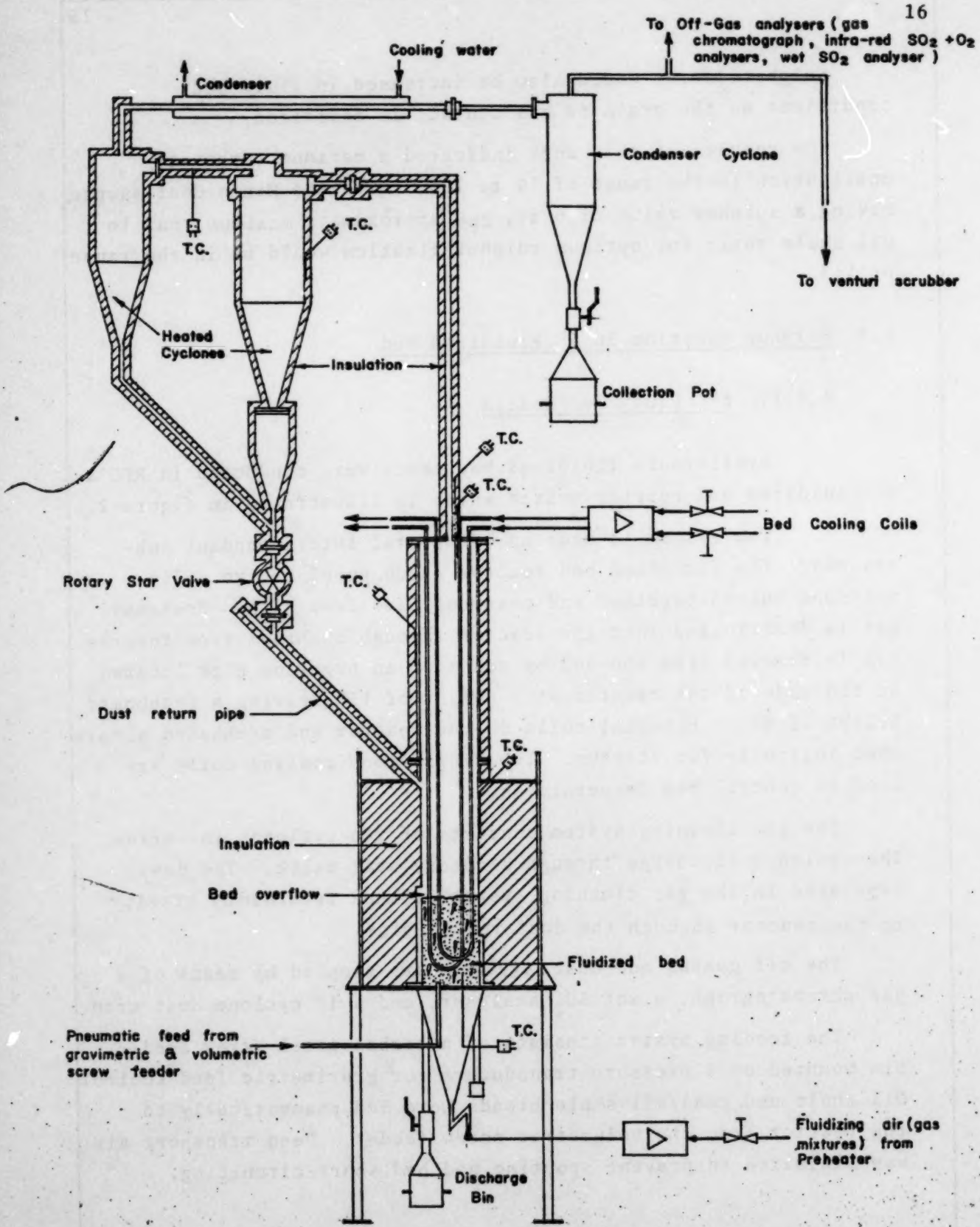


Fig. 2 SCHEMATIC VIEW OF THE R.P.C. 6 in. DIAMETER FLUIDIZED BED REACTOR

The reactor freeboard, cyclones and return pipe all have external heaters to maintain gas temperatures in excess of 500°C.

The fluid bed, freeboard, cyclone and outside wall temperatures are all monitored by means of type K thermocouples.

4.4.2. Preliminary Oil Shale Combustion Trials

Preliminary fluid bed combustion trials were undertaken on the minus 50 mesh 25 gal/ton bulk oil shale sample for which analyses are given in Table 1. Roaster operating conditions of 800°C, rate of 2 kg/hr., and 10% air (oxygen) were employed. These conditions resulted in a retention time of 1.4 hours and a spacial velocity of 23 cm/sec. Assumed combustion stoichiometry used for O_2 requirements for combustion were as follows:

$$CH_2 + 1.5\ O_2 \longrightarrow CO_2 + H_2O$$

$$FeS_2 + 2.7\ O_2 \longrightarrow 0.5\ Fe_2O_3 + 2SO_2$$

Greater than 95% of the ash was collected in the bed overflow and the cyclone trap, while < 5% was carried over to the venturi scrubber. The ash contained no detectable residual organic carbon based on weight loss tests at 800°C in presence of excess oxygen. The oil shale exhibited excellent fluidization characteristics and the bed temperature of 800°C was maintained without any external heating. In fact, an excess of heat was produced and considerable cooling water(2-3 litres/hour) was required. As a check on the combustion air requirement, once bed equilibrium was established, the feed was slowly increased to 2.2 kg/hr where the bed temperature maximized and thus agreeing the calculated O_2 requirement.

4.4.3. Sulphitization in 6" Reactor

SO_2 fixation capacities of Albert County Oil Shale in a fluidized reactor were determined by passing various SO_2

and fluidization air mixes through the 6" reactor with a 25 gal/ton oil shale bed and feed rate of 2 kg/hr. The inlet and outlet gasses were analyzed for their SO_2 strengths. The results are illustrated in figure 3. The maximum SO_2 fixation was 5.4 grams of SO_2 per 100 grams of fresh oil shale. The bulk Minto Coal sample averaged 6.8% sulphur and thus for complete fixation, a ratio of oil shale to coal of 2.5 to 1 would be required.

4.5 Coal/Oil Shale Combustion Trials

A blend of 1 part of minus 8 mesh Minto Coal to 3 parts oil shale was prepared for initial combustion tests in the 6" fluid bed reactor.

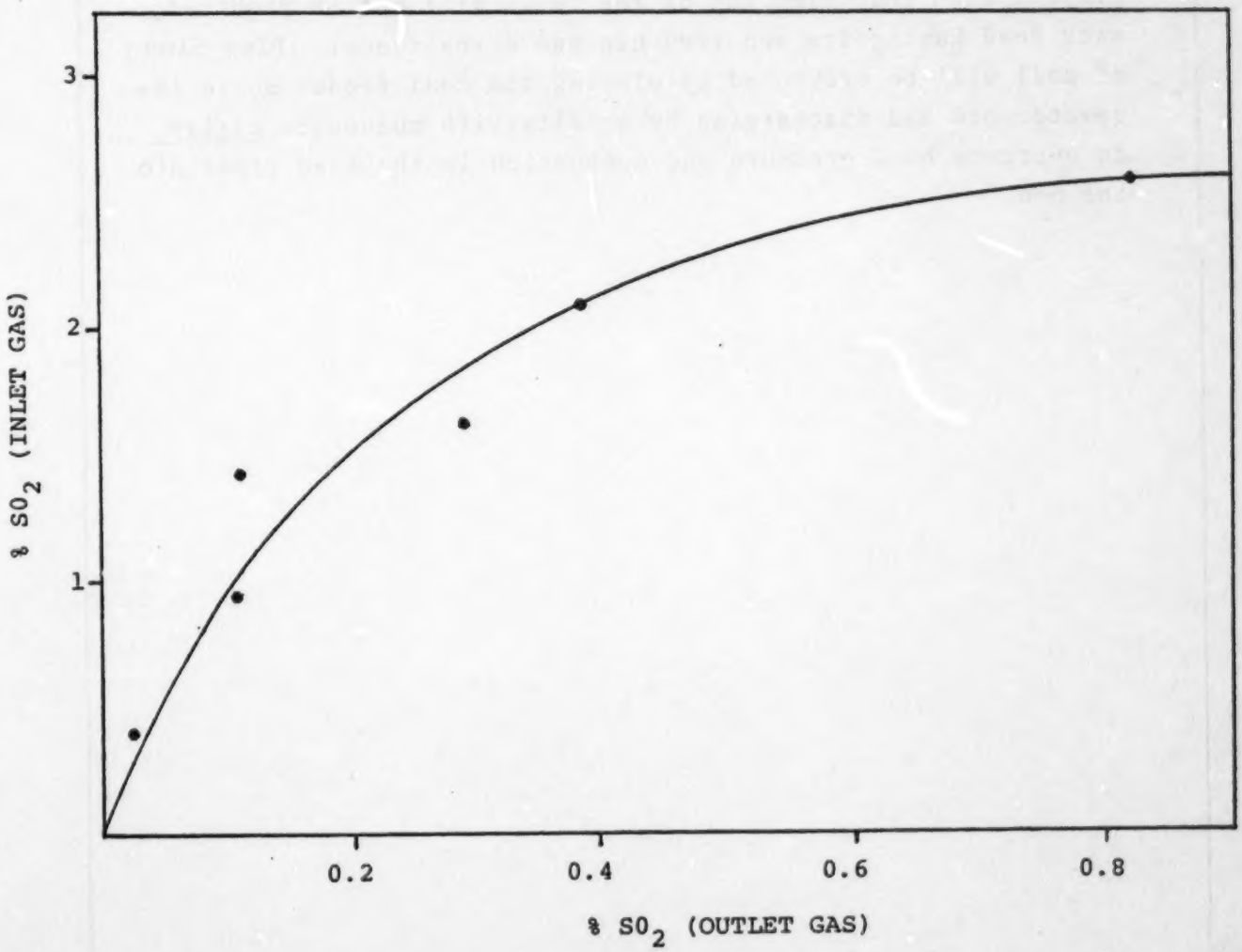
A feed rate of 1.25 kg/hr. was chosen, giving a retention time of 2.3 hours. An excess of 10% O_2 was used for combustion resulting in a spacial velocity of 27 cm/sec at 800°C. The bed temperature was maintained at 800°C by means of the two internal cooling coils. Considerably more cooling water (5-15 litres/hours)was required with the addition of coal to the feed. These wide fluctuations in the cooling water requirement were indicative of a problem with the feeding system resulting in plug feeding of the coal.

Fluidization characteristics were excellent and ash carryover to the scrubber tank was minimal. Fluidization was also enhanced by the coal ash residue which formed light porous pellets. These pellets which remain in the fluid bed are not carried over to the gas cleaning system and are discharged by means of an overflow pipe, thus reducing the overall cyclone ash handling requirement.

The off-gas was monitored for its SO_2 strength by means of a wet SO_2 absorption analyses. A calculated SO_2 gas strength produced by the coal combustion with no fixation would have been 0.58%. No SO_2 was detected, with limits of detection being 0.05%. In future testing the SO_2 off-gas strength will be monitored with a gas chromatograph having a SO_2 detection limit of 0.01%. NO_x

FIGURE 3

SO_2 FIXATION ON VARIOUS SO_2 GAS STRENGTHS IN 6" FLUIDIZED BED REACTOR



emmissions will also be monitored.

Some problems occurred in feeding the blended coal and oil shale together and were probably due to the high electrostatic nature of the coal or it's contained moisure which average about 4.4% H_2O. Modifications are being made to the coal and oil shale feeding systems for the next phase of the project such that blending of the feeds will not be required, each feed having its own feed bin and screw feeder. Plug flow of coal will be prevented by placing the coal feeder above the reactor bed and discharging by gravity(with pneumatic assist to overcome back pressure and combustion in the feed pipe)into the bed.

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Report approved by: R. S. Boorman

APPENDIX A1

Methods of SO_2 Analyses in Reactor Inlet and Outlet Gases

SO_2 in the gas was measured by means of a wet absorption analyses and an analytical gas chromatograph. Gas samples were drawn from inlet and outlet off-gas streams by means of a Masterflex peristaltic pump through a Matheson 601 flowmetre to either two absorption impingers or the gas chromatograph and finally to a dry gas metre.

Using a series of SO_2 and O_2 gas mixtures from standard gas bottles and dilutions with N_2, standardization curves for both SO_2 and O_2 were established for the gas chromatograph. Gases tested ranged from 0.1 to 9% for SO_2 and 0.25 to 21% for O_2. The plots are illustrated in figures A1-1 and A1-2. A sample gas chromatograph trace for various SO_2 standards are given in Fig. A1-3. Although these curves were not used for the preliminary testing due to a failure in the temperature control switch in the gas chromatograph during that time, they will be used extensively in further tests.

In the wet SO_2 analyses the gas stream was passed through a 0.2N NaOH-3% HOOH scrubber solution. SO_2 is absorbed and the peroxide oxidizes the SO_2 to SO_3. The $BaCl_2$-Thorin indicator titration method was used after boiling to remove peroxide and cation exchange to remove metal ions, to determine total sulphate and calculate SO_2 content.

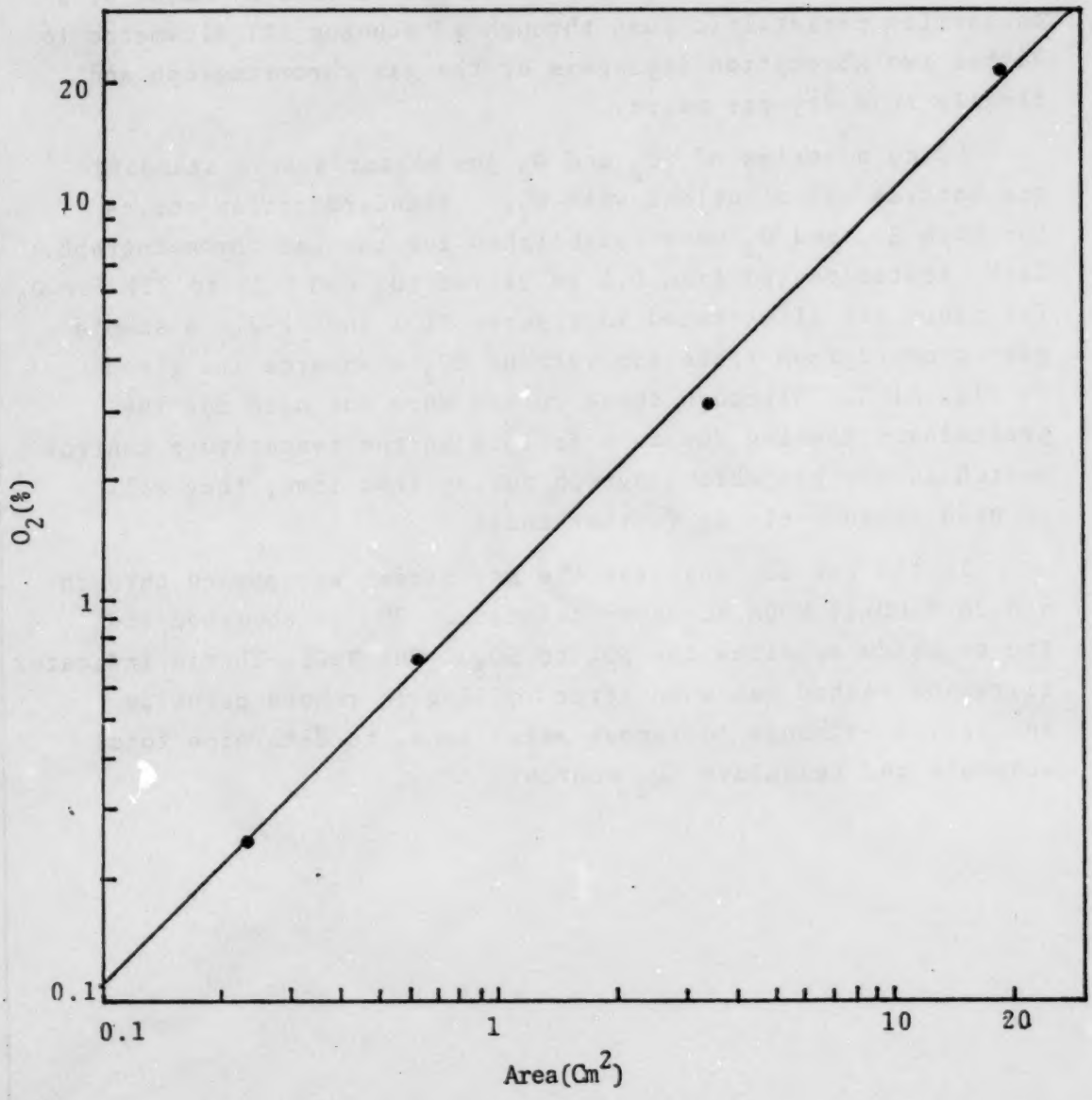


FIG. A1-1 Gas Chromatograph Oxygen %/Curve Area from Standard Gas Mixes(Attenuation = 16, Flow Rate = 40 cc/min)

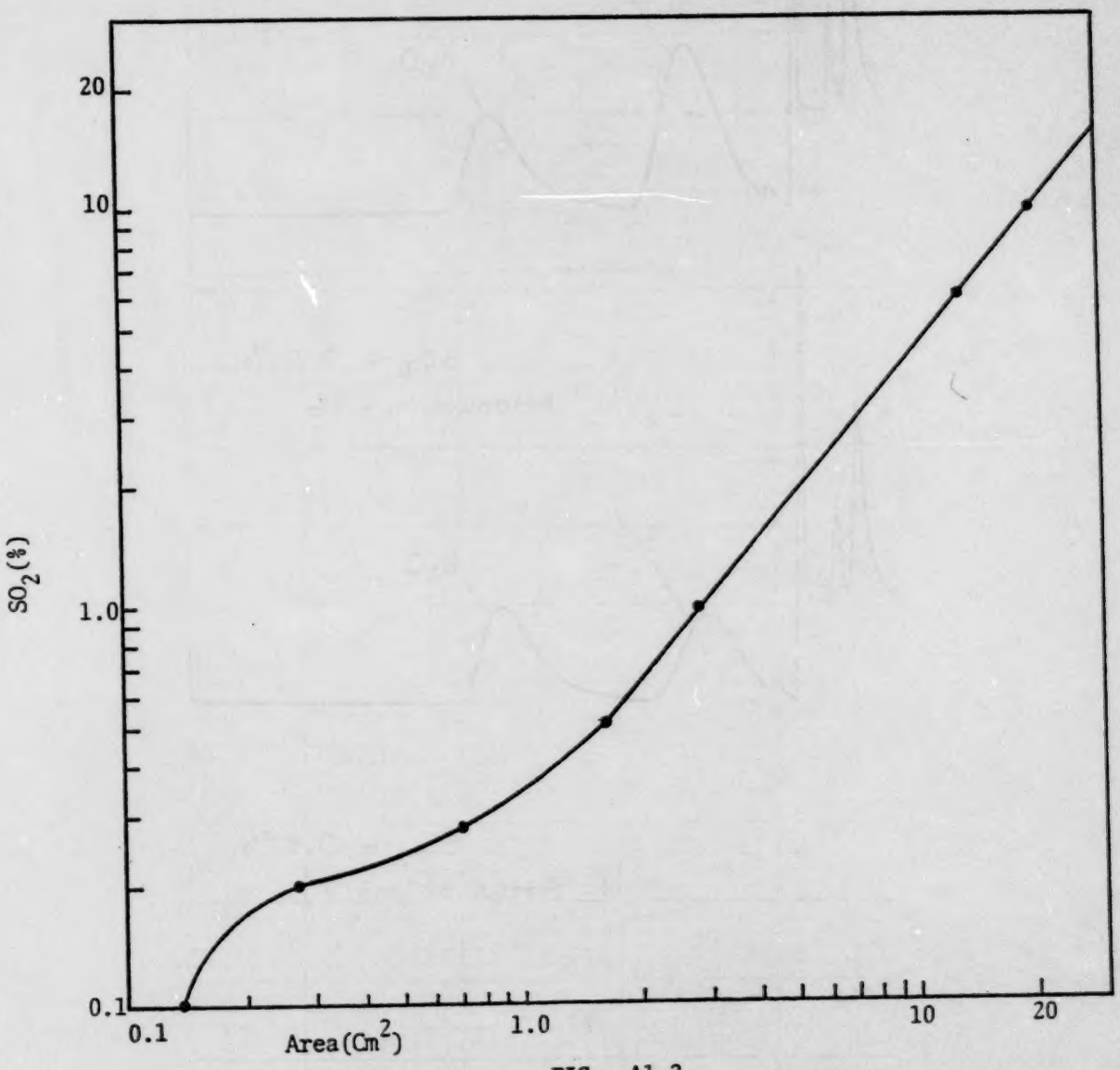


FIG. A1-2

GAS CHROMATO GRAPH SO_2 %/CURVE AREA FROM STANDARD MIXES(ATTENUATION = 16, FLOW RATE = 40 cc/min).

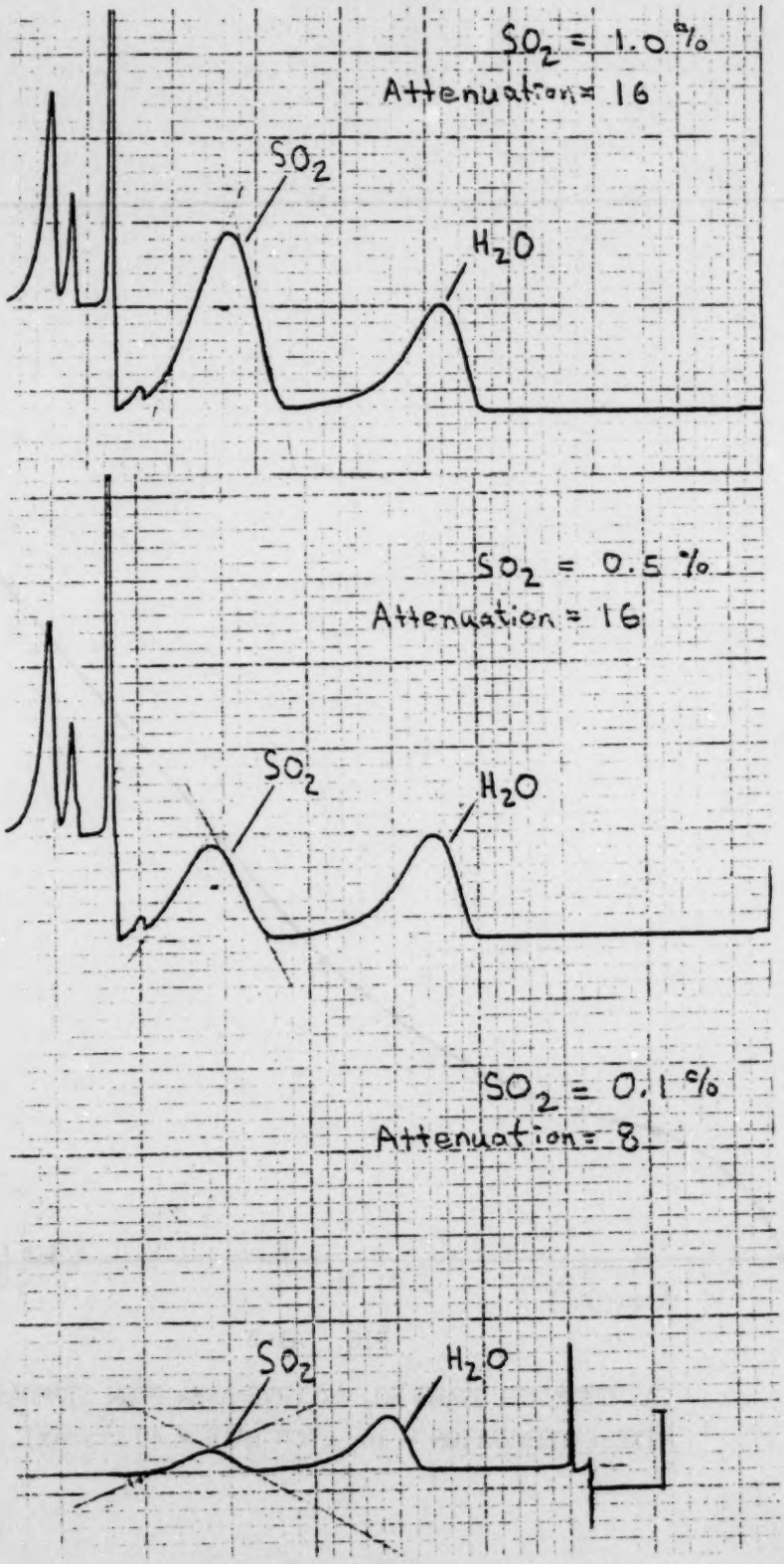


FIG. A1-3

GAS CHROMATOGRAPH STANDARD CURVES FOR SO_2

APPENDIX A2

Preliminary Comparison of Alternative Strategies for Coal and Oil Shale Utilization

INTRODUCTION

This appendix is an evaluation and comparison of three alternatives for generating thermal energy and shale oil by burning New Brunswick Coal, using 10 gal/ton Albert County Oil Shale to capture SO_x emmissions in compliance with environmental standards.

PROCESS DESCRIPTIONS

ALTERNATIVE A SIMPLE FLUIDIZED BED COMBUSTION OF COAL/SHALE MIXTURES

Coal and oil shale mixtures are charged to a fluid bed reactor and burned in air entering at 25°C. The bed temperature is maintained at 800°C. Steam is generated by heat exchanger coils in the bed. A process flow sheet is shown in Figure A2-1. Materials and heat balances are summarized in Table A2-1.

Basic stoichiometric and thermochemical data used in deriving the materials and heat balances are presented in Appendix 3.

The system is simple but wastes energy due to the large mass of gas entering the system at 25°C and leaving at 800°C. The mass of fine ash and spent shale for disposal is about 16 times the weight of fly ash to be handled in a conventional coal fired system. Gas cleaning and waste disposal costs are therefore to be expected to be abnormally high compared with conventional coal fired power stations.

FIGURE A2-1

PROCESS FLOWSHEET

ALTERNATIVE A SIMPLE FLUIDIZED BED COMBUSTION OF COAL/SHALE MIXTURES

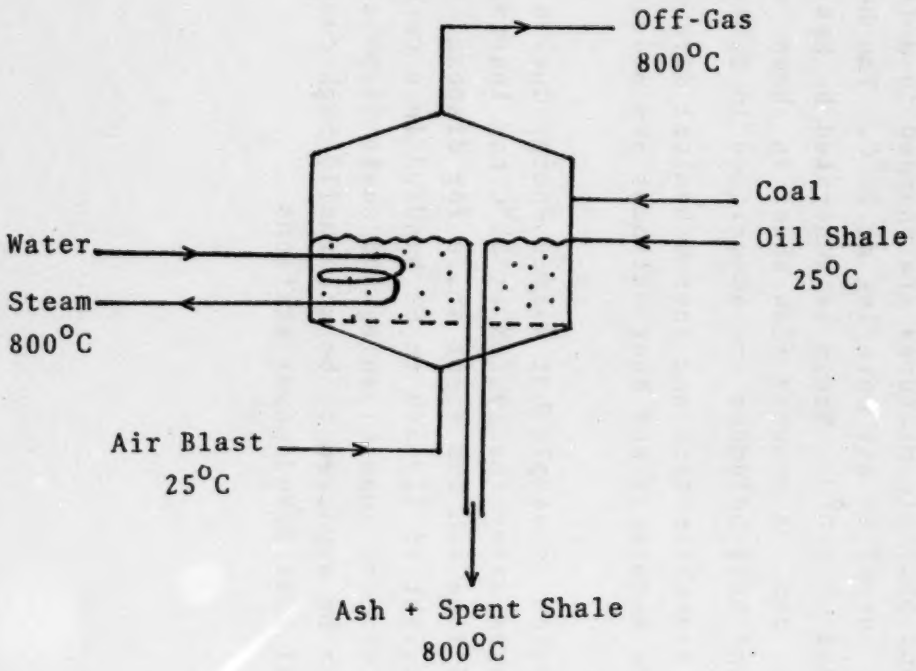


TABLE A2-1

MASS AND HEAT BALANCE SUMMARY - ALTERNATIVE A

BASIS: - PER TONNE OF COAL BURNED

	TONNE	Nm^3	
COAL TO FB FURNACE	1.00		
SHALE TO FB FURNACE	3.00		
AIR BLAST	12.36	9603	
COAL ASH @ 800°C	0.20		
SPENT SHALE @ 800°C	3.00		
OFF-GAS @ 800°C	13.07	9762	
AVAILABLE HEAT FOR STEAM RAISING @ 800°C			4.5×10^6 KCal
SHALE OIL PRODUCED	NONE		

ALTERNATIVE B FLUIDIZED BED COMBUSTION OF COAL/SHALE MIXTURES WITH AIR PREHEAT.

In alternative B thermal economies are effected by discharging hot ash and shale through a second fluid bed below the fluid bed combustion chamber (Figure A2-2). Materials and heat balances are summarized in Table A2-2.

The insertion of the fluid bed heat exchanger results in an increase in steam raising capacity by 11% over case A. Ash and spent shale are discharged at 179°C instead of 800°C thus handling problems are greatly reduced. However gas cleaning and waste disposal costs are still going to be high because of the large amount of solid waste material to be handled.

FIGURE A2-2
PROCESS FLOWSHEET

ALTERNATIVE B SIMPLE FLUIDIZED BED COMBUSTION OF COAL SHALE MIXTURES WITH AIR PREHEAT

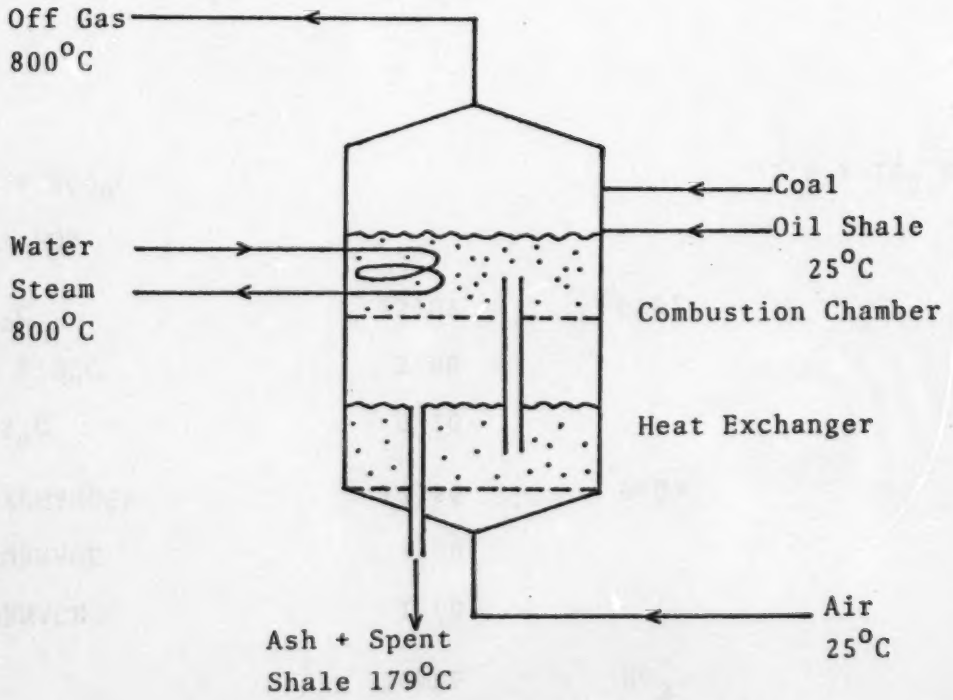


TABLE A2-2

MASS AND HEAT BALANCE SUMMARY ALTERNATIVE B
BASIS: - PER TONNE OF COAL BURNED

	TONNE	Nm^3	
COAL TO FB FURNACE	1.00		
SHALE TO FB FURNACE	3.00		
AIR TO HEAT EXCHANGER	12.36	9603	
COAL ASH @ 179°C	0.20		
SPENT SHALE @ 179°C	3.00		
OFF GAS @ 800°C	13.07	9762	
AVAILABLE HEAT FOR STEAM RAISING @ 800°C			5.0×10^6 KCal

ALTERNATIVE C INTEGRATED FLUID BED COMBUSTION OF COAL WITH FLUID BED RETORTING OF OIL SHALE

Figure A2-3 shows a system in which hot off gas from a fluid bed coal combustion system is cooled and desulphurized by reacting it with oil shale in a double hearth fluid bed reactor. In the upper bed of the oil shale reactor oil is distilled off at 500°C. It is assumed that 75% of the hydrocarbon is removed by this process. Partially retorted shale at 500°C then passes down into a second fluid bed hearth where it is heated to 709°C by off gas from the coal burner at 800°C. In this reactor off gas is desulphurized by the oil shale and residual oxygen in the off gas is combined with residual hydrocarbon in the oil shale thus removing the possibility of oxidizing the more volatile hydrocarbon in the retort.

The amount of shale which can be processed within the constraints of the assumed retorting temperature of 500°C and the combustion requirements of the coal at 800°C is calculated by thermal balances to be 5.2 TONNES PER TONNE OF COAL. Thus more efficient off gas desulphurization is to be expected than in the foregoing cases because roughly 75% more oil shale is processed.

The hot oil shale(709°C)passes to an air preheater where it is cooled to 120°C for final discharge by cold combustion air for the coal burner.

The mass and heat balance summary is presented in Table A2-3. This balance shows that about a barrel of oil per tonne of coal burned can be derived from the oil shale by off gas cooling. Fly ash handling problems could be minimized in this system by charging a relatively coarse oil shale feed to the retort. This would also reduce the energy required in pulverizing the shale to be compatible with fluidizing in a coal burner.

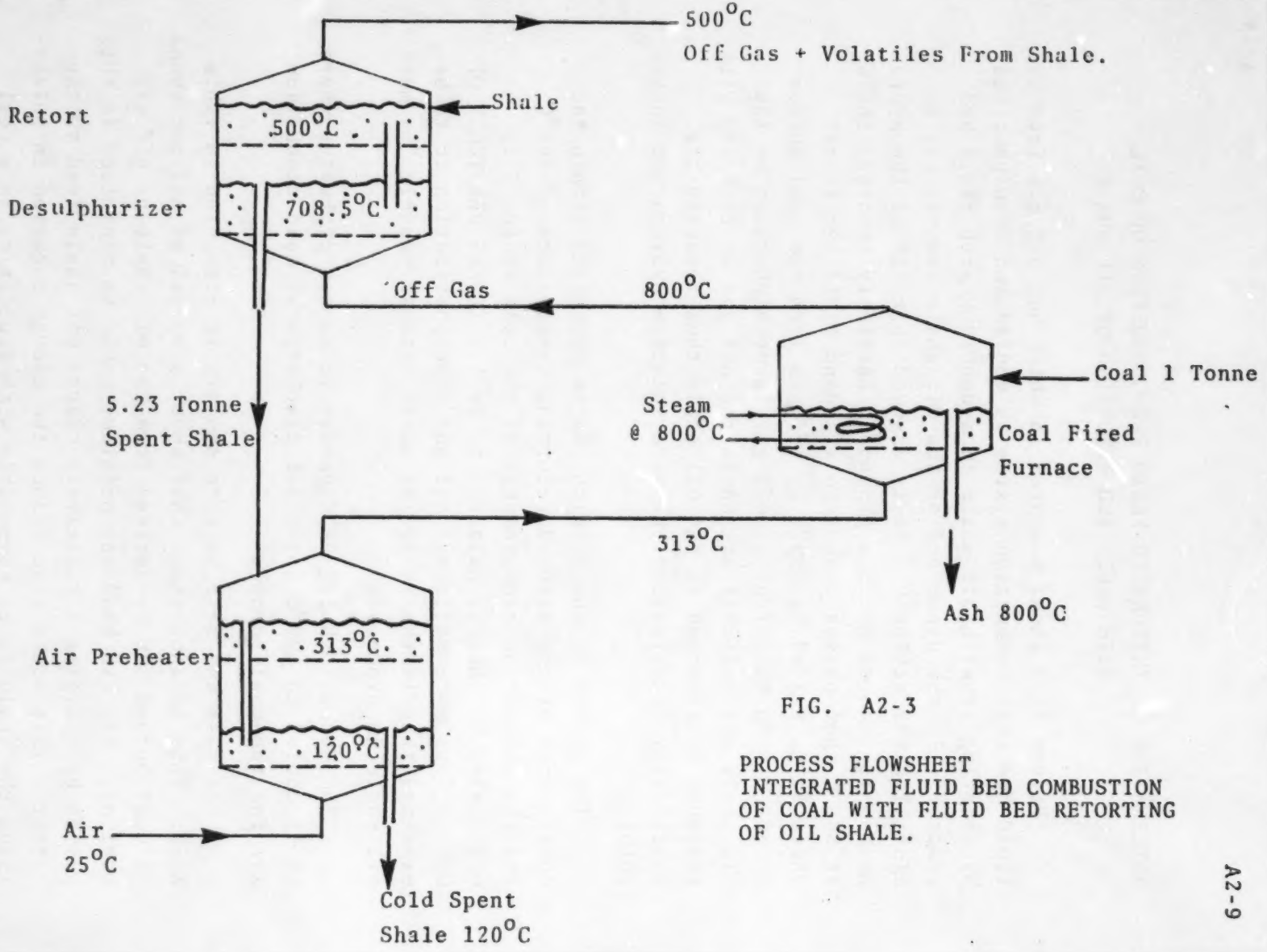


FIG. A2-3

PROCESS FLOWSHEET
INTEGRATED FLUID BED COMBUSTION
OF COAL WITH FLUID BED RETORTING
OF OIL SHALE.

TABLE A2-3

MASS AND HEAT BALANCE SUMMARY ALTERNATIVE C
BASIS: - PER TONNE OF COAL BURNED

	TONNE		Nm^3	
COAL TO FB FURNACE	1.00			
SHALE TO RETORT	5.23			
AIR TO HEAT EXCHANGER	10.43		8100	
COAL ASH @ 800°C	0.20			
SPENT SHALE @ 120°C	5.2			
OFF GAS @ 500°C	11.00		8158	
CONDENSIBLE OIL VAPOUR	0.16	=	1.15 BBL	
AVAILABLE HEAT FOR STEAM RAISING @ 800°C				5.0×10^6 KCal

By separating the oil shale processing plant from the coal burning plant it would be possible in principle to combine an existing coal fired plant with a shale oil reactor system for off gas desulphurization, oil production, and air preheating.

Assuming a scale of approximately 11,500 BBL of oil per day, alternative C would involve mining and burning 10,000 tons/day of coal and 53,000 tons/day of oil shale. From the mining standpoint these production rates are similar to ore production rates from a typical prophyry copper mine. If the steam produced is to be used solely for electrical power generation then, at 30% conversion efficiency, it would be sufficient to drive an 1,000 Mw power station.

COMPARISON OF ALTERNATIVES

There are, of course many variants of the alternatives proposed in this study. However, most fall into two basic design categories. In the first, oil shale and coal are mixed and processed together (eg. alternatives A and B). In the second, shale and coal are processed in two separate processing trains linked only by supply of intermediate products from the one train to the other. (Alternative C). Although this latter alternative appears to be more capital intensive at first because of the two processing trains, it is more flexible and requires less ancillary equipment for such purposes as off gas cleaning and ash disposal. Principal advantages are:

1. Shale treatment train can be retrofitted to conventional coal burning power plant.
2. Shale treatment train would eliminate the need for a SO_x scrubber in a conventional coal burning power plant.
3. Shale could be processed in a relatively coarse state, thereby eliminating problems of off gas dust removal and disposal of large quantities of fine ash.

4. Separation of shale processing from coal processing reduces the tendency for low melting clinker formation and renders the ash products more amenable to processsing into pozzolanas or for biproduct metal recovery.

APPENDIX A3
Exploratory Calculations

A3.1 OIL SHALE/COAL AND LINESTONE/COAL RATIOS

1. Ratio of shale/coal needed to fix 85% sulphur in coal.

Ref Doyle Babcock, Wilcox 1980

$M_{CaO}/M_S = 2.5:1$

For Doyle this corresponded to

W_{shale}/W_{coal} of about 1:1

ie. % CaO in shale was 15%

S in coal was 3.5%

Applying same logic to NB shale(say 10% CaO)and Minto Coal(say 7% S).

$M_{CaO}/M_S = 2.5:1$ as before

or $M_{CaO} = 2.5 \times M_S$

$$M_{CaO} = W_{shale} \times \frac{.10}{56} = 2.5\, M_S$$

$$M_S = W_{coal} \times \frac{.07}{32}$$

$$\therefore W_{shale}/W_{coal} = 2.5 \times \frac{0.07}{32} \times \frac{56}{.10} = 3.06$$

(NB: of % CaO in shale = 20% W_{shale}/W_{coal} is 1.53).

2. Ratio of limestone/coal needed to fix 95% sulphur

Ref Doyle Fig.5

$M_{CaO}/M_S = 4.0:1$

For 92% $CaCO_3$ in limestone 3.5% S in coal.

$$M_{CaO} = M_{CaCO_3} = W_{LS} \times \frac{.92}{100}$$

$$M_S = W_{coal} \times \frac{.035}{32}$$

$$\therefore W_{LS}/W_{coal} = 4 \times \frac{035}{32} \times \frac{100}{92} = 0.48$$

For Minto coal(7% S)

$$W_{LS}/W_{coal} = 4 \times \frac{07}{32} \times \frac{100}{92} = 0.95$$

A3.2 HEAT BALANCES

A. Combustion of coal

Assumptions

Proximate analysis of Minto Coal.

Ash	20.5%
Fixed carbon	52.0
Sulphur	7.7
Volatiles	19.8

Combustion Stoichiometry

Fixed C + $O_2 \longrightarrow CO_2$

Sulphur vs FeS_2

$$FeS_2 + 3.75\ O_2 \longrightarrow 0.5\ Fe_2O_3 + 2SO_3$$

Volatiles are $(CH_2)_n$

Basis per 100 kg dry coal.

Combustion of fixed carbon

$$\frac{52}{12}\ C + \frac{52}{12}\ O_2 \longrightarrow \frac{52}{12}\ CO_2 \text{ (Kg. mols)}$$

Combustion of pyrite

$$\frac{7.7}{64}\ FeS_2 + 3.75 \times \frac{7.7}{64}\ O_2 \longrightarrow \frac{7.7}{2X64}\ Fe_2O_3 + \frac{2X7.7}{64}\ SO_3$$

Combustion of Volatiles

$$\frac{19.8}{14}\ H_2 + \frac{19.8}{14X2}\ O_2 \longrightarrow \frac{19.8}{14}\ H_2O$$

$$\frac{19.8}{14}\ C + \frac{19.8}{14}\ O_2 \longrightarrow \frac{19.8}{14}\ CO_2$$

Stoichiometric O_2 (kg. mols)

$4.33 + 0.45 + 0.71 + 1.41 = 6.9$

Assume 10% excess

$$N_2 = 7.59 \times \frac{79}{21} = 28.57$$

Off Gas		% v/v
O_2 =	0.69	1.88
N_2 =	28.57	77.93
CO_2 =	4.33 + 1.41 = 5.75	15.68
SO_3 =	0.24	0.65
H_2O =	1.41	3.85

TOTAL 36.66 Kg mols per 100 Kg dry coal.

Stoich O_2 required	O_2 required(moles)
Fixed C = $\frac{0.52}{12}$ = 043 moles =	0.043
Pyrite = $\frac{0.077}{64}$ = .0012 moles FeS_2 =	0.0045
Volatiles = .198 X 1/1.17 X 1/12 =	0.0141
H_2 = .198 X 1/1.17 = .0144 moles H_2=	0.0072
TOTAL O_2 =	0.0688

Off Gas

CO_2 = .043 + 0141 =	0.0571
SO_3 =	0.0024
H_2O =	0.0144

1.2 Stoich

N_2 = 1.2 X .0688 X $\frac{79}{21}$	0.3106
O_2 =	0.0138

Coal-Available Heat

	Moles	$H_{800}/-H_{25}/$ Moles		K Cal.
N_2	.3106	5.8×10^6	=	1.80×10^6
O_2	.0138	6.1×10^6	=	8.4×10^4
CO_2	.0571	9.0×10^6	=	5.14×10^5
SO_3	.0024	12.5×10^6	=	3.00×10^5
H_2O	.0144	7.1×10^6	=	1.02×10^5
TOTAL	3.98×10^{-1} TM_3			
	8.92×10^3 Nm			
Ash	.205 Ton - 19.38×10^3/Ton		=	3.97×10^4
TOTAL			=	2.57×10^6

L C V = 6.60×10^6 K Cal/Ton.

N A V = 6.6 - 2.6 = 4.0×10^6 K Cal/Ton.

L S T per ton = $-.19 \times 10^6$ K Cal/Ton.

B. Oil Shale

Say 10 gal/ton @ 1.09×10^6 K Cal/Tonne.

S.G. oil = .88

Kg oil/ton - 100 X .88 X .454 = 40 Kg.

Assume oil is hydrocarbon = $2H/C$

$W_H/W_C = 2/12 = 1/6$

$W_H + W_C = 40$

$W_C = 40/1.17 = 34.3$ Kg = .00286 Moles/Ton.

Moles H_2 = .00286

O_2 require = .00286 + .00143 = 4.286×10^{-3} Moles/Ton

Per Tonne Shale. Off Gas

		K Cal.
1.2 Stoich O_2 =	5.14×10^{-3} moles	
N_2 =	1.93×10^{-2} moles	1.11×10^5
O_2 =	8.57×10^{-4} moles	5.23×10^3
CO_2 =	2.86×10^{-3} moles	2.57×10^4
H_2O =	2.86×10^{-2} moles	2.03×10^4
TOTAL =	3.10×10^{-2} moles	1.63×10^5
Ash =	695 Nm_3	1.93×10^5
TOTAL =		3.57×10^5

L C V = 1.09×10^6 K Cal/Ton - 3.57×10^5 K Cal/Ton

Net avail. ash heat(slab) is $.733 \times 10^6$ K Cal/Tonne.

A3.3 COMBUSTION CHARACTERISTICS OF COAL AND OIL SHALE

A. Coal Combustion @ 800°C

Per 1000 Kg coal

10% excess O_2

Air

O_2 = 75.9 Kg mol. = 8100 Nm^3/Tonne.

N_2 = 285.7 Kg mol.

Off Gas

O_2 = 6.9 Kg mol.

N_2 = 285.7 Kg mol.

CO_2 = 57.5 Kg mol.

SO_3 = 2.4 Kg mol.

H_2O = 14.1 Kg mol.

Low Cal Val. = 6.6 X 10^6 K Cal.

Heat Capacities 1.Combustion Air = -2680 K Cal/Deg C.

2.Ash = -51.25 K Cal/ Deg C.

(20.5% in Coal = .205 Tonne)

3.Off Gas = -3021 K Cal/Deg C.

B. Oil Shale Combustion

Per 1000 Kg oil shale

39.9 Kg$(CH_2)_n$

10% excess O_2

Air

O_2 = 4.71 Kg mol.

N_2 = 17.72 Kg mol. = 502.4 N_m^3/Tonne

Off Gas

O_2 = 0.43 Kg mol.

N_2 =17.72 Kg mol.

Co_2 = 2.85 Kg mol.

H_2O = 2.85 Kg mol.

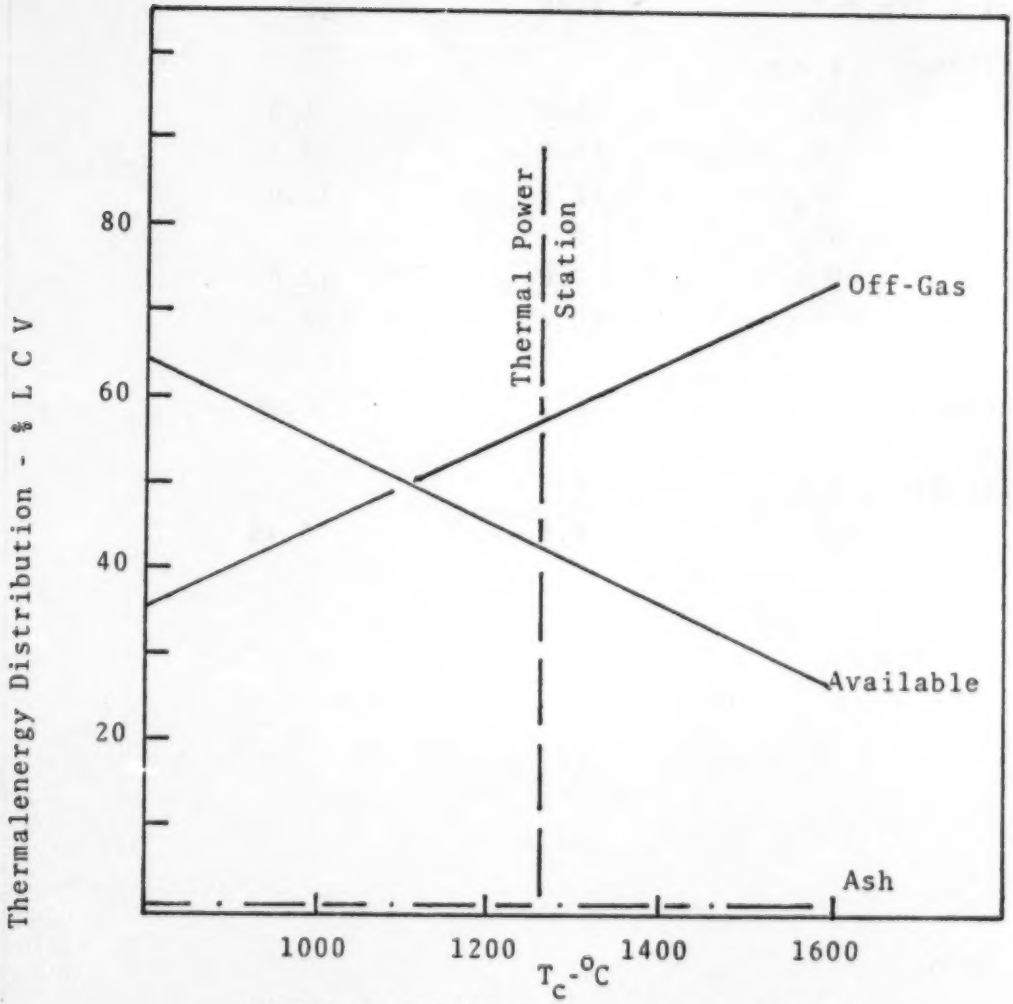
Low Cal Val = 4.33×10^5 K Cal.

Heat Capacities

1. Combustion Air = -166 K Cal/Deg C.
2. Off Gas = -199 K Cal/Deg C.
3. Ash = - 240 K Cal/Deg C.

A3.4 SUMMARY

		Per Tonne Fuel	
		Coal	Oil Shale
Combustion Air	Nm^3	8100	502
Off Gas Comp^n	% v/v		
	O_2	1.9	1.8
	N_2	77.9	74.2
	CO_2	15.7	12.0
	SO_3	0.7	-
	H_2O	3.8	12.0
		100.0	100.0
Ash Tonnes		0.2	0.96
Low Calorific Value	$\frac{K\ Cal}{10^6}$	6.6	0.43

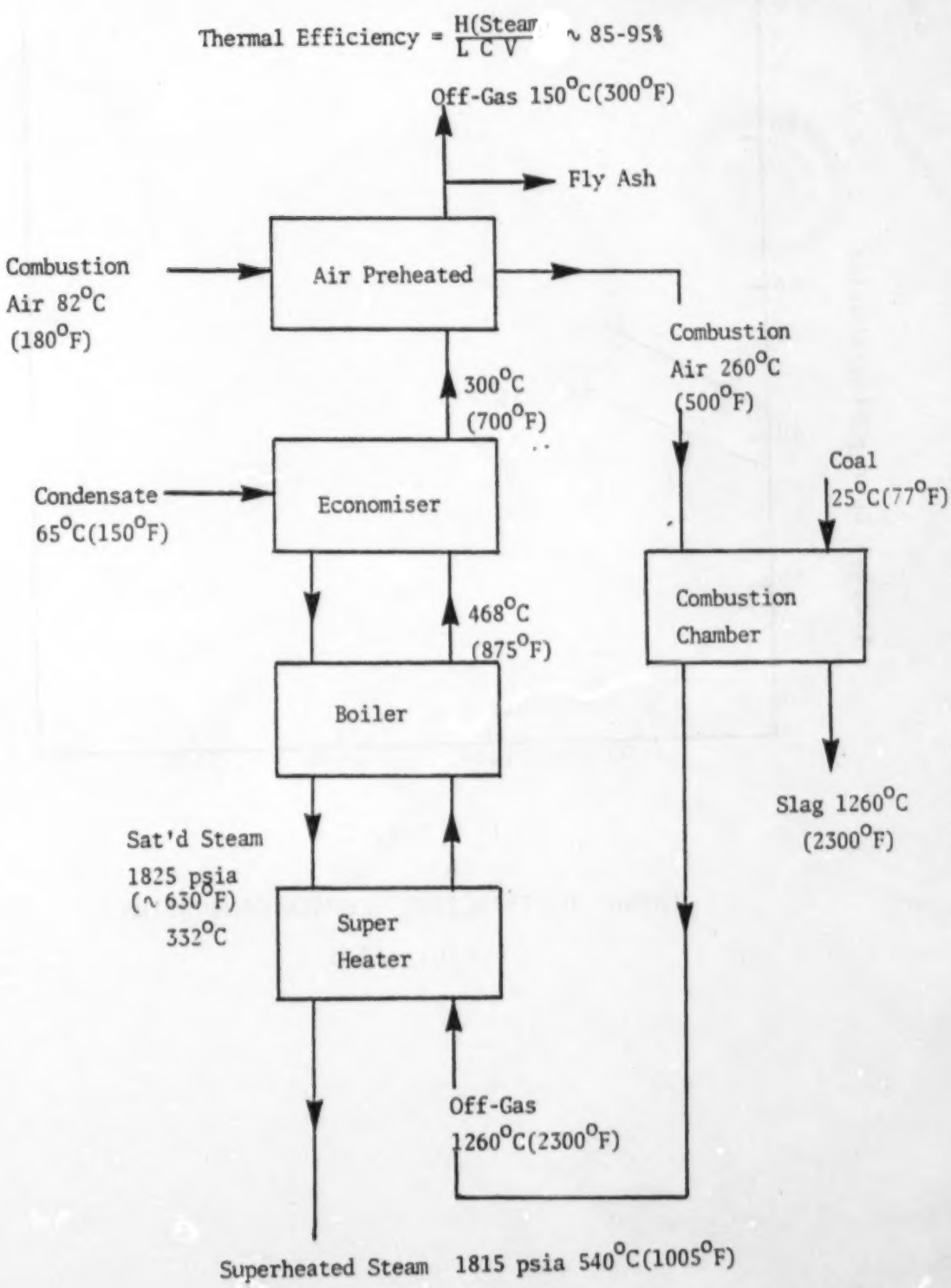


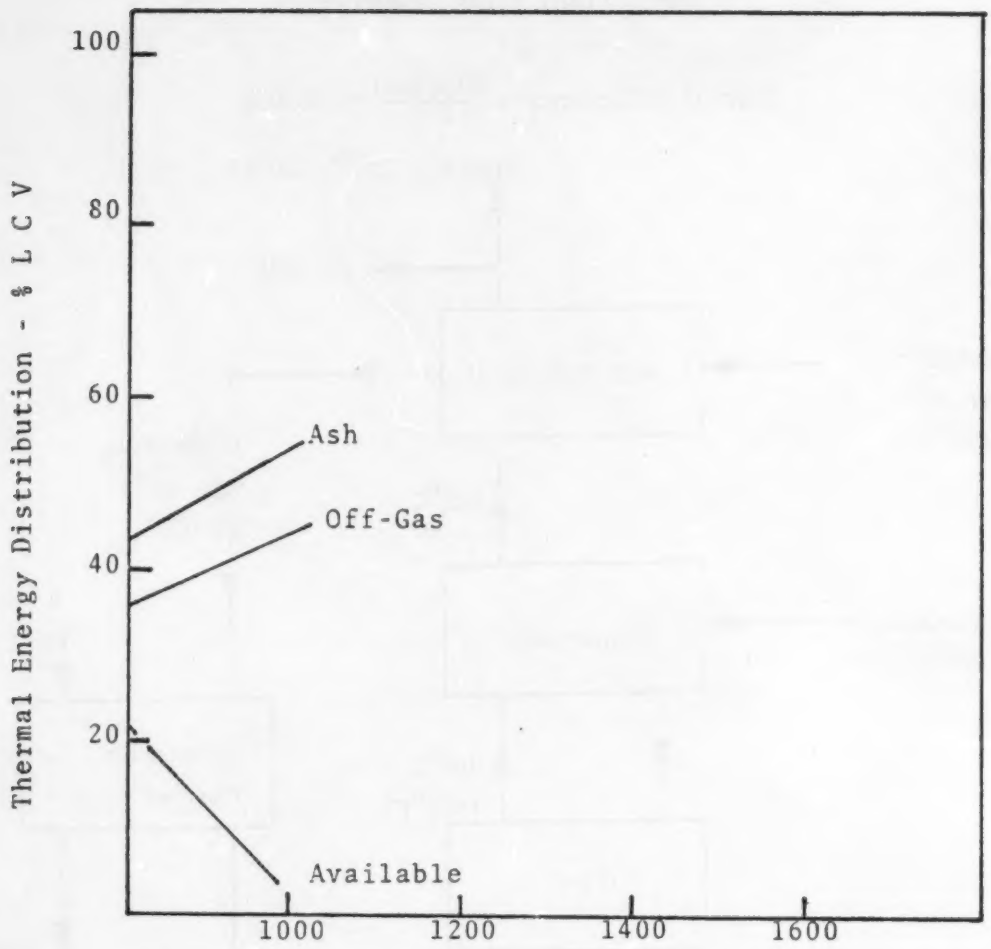
ENERGY DISTRIBUTION - COAL COMBUSTION

FIG. A3-1

FIG. A3-2

PROCESS FLOWSHEET - TYPICAL COAL FIRED POWER PLANT STEAM GENERATOR





ENERGY DISTRIBUTION - SHALE COMBUSTION

FIG. A3-3

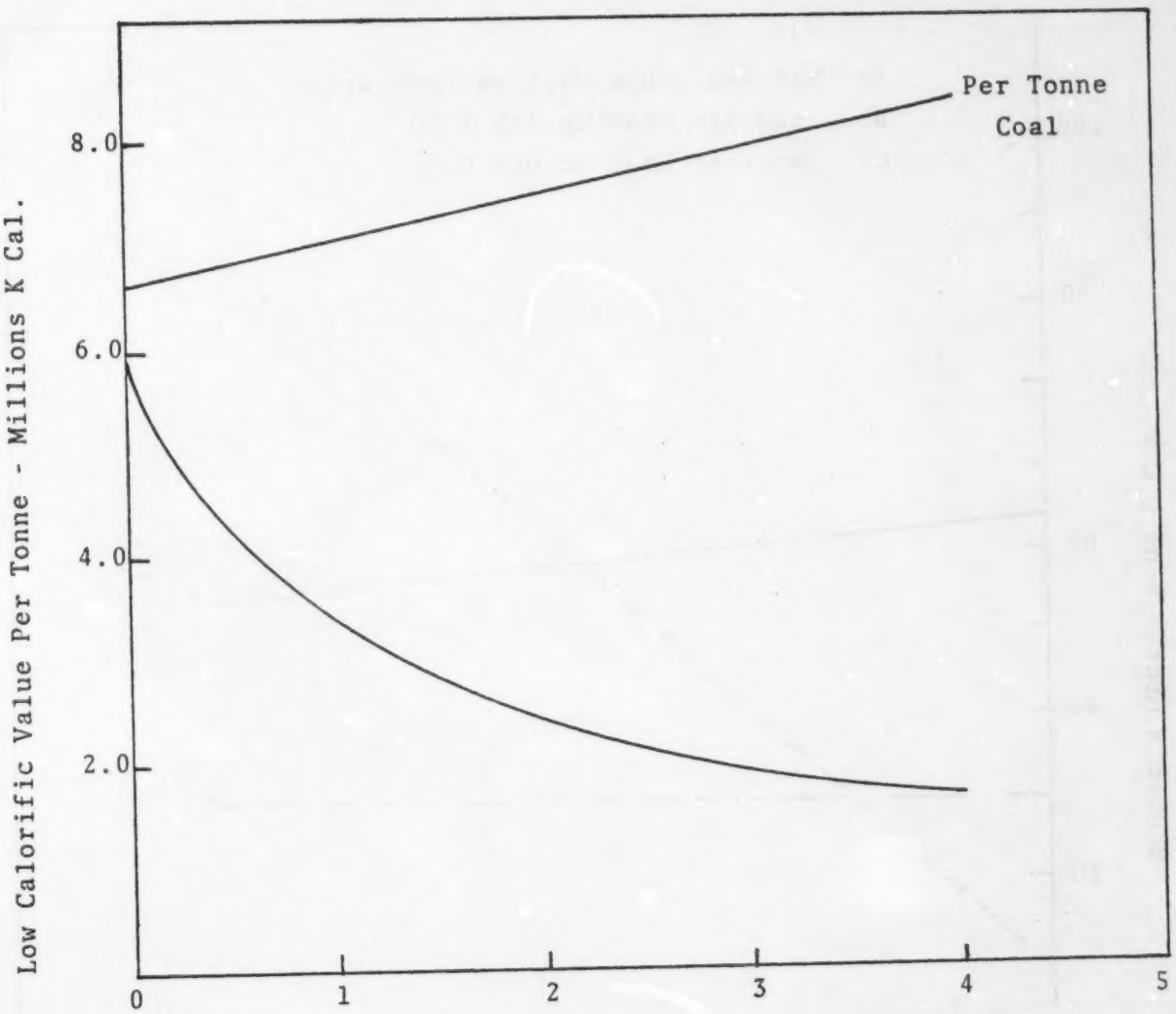


FIG. A3-4

LOW CALORIFIC VALUES PER TONNE COAL AND COAL + SHALE

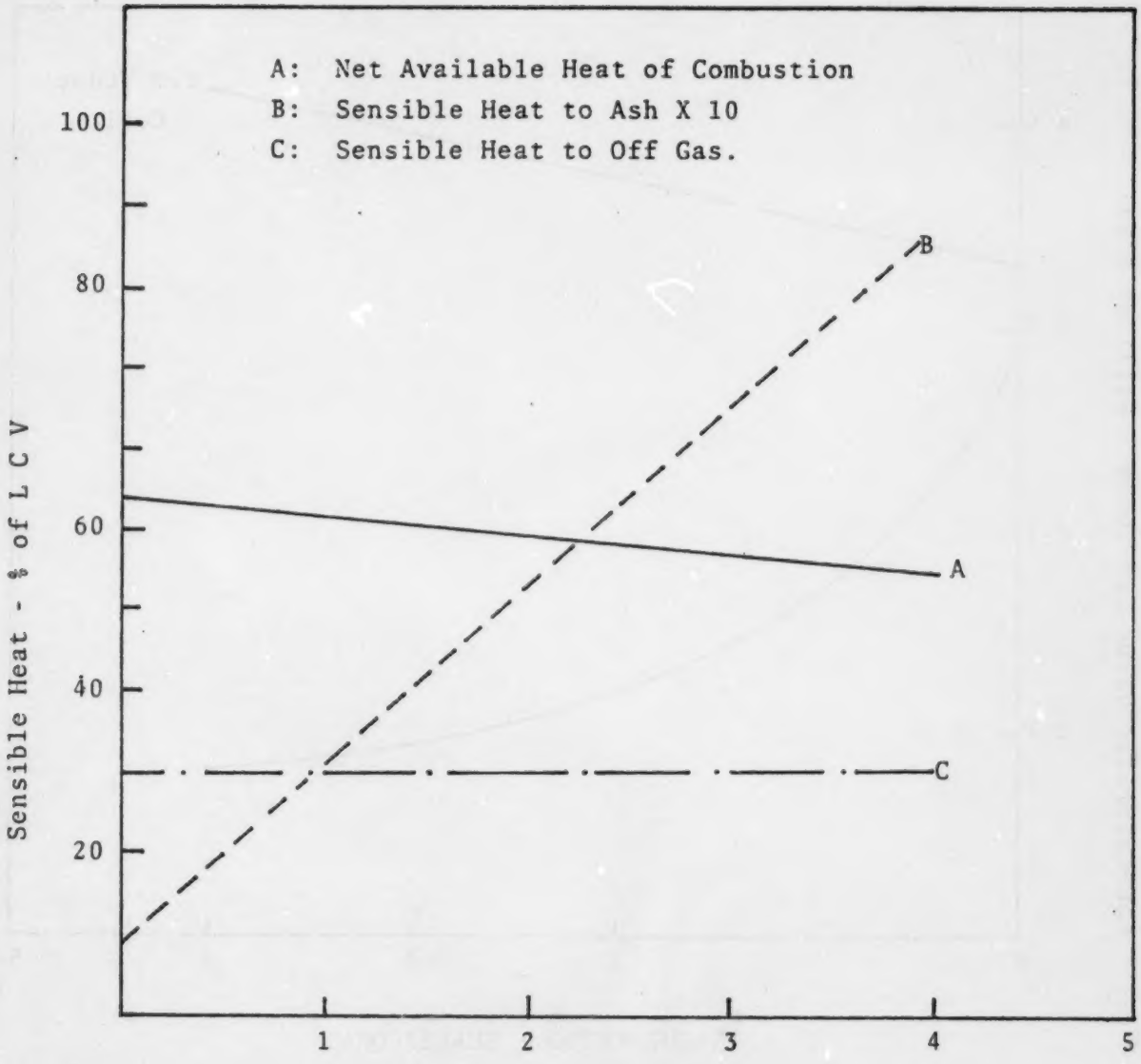


FIG. A3- 5

SENSIBLE HEAT GENERATED IN F B R.